

# **Appendix GG**

## **An Analysis of VOC Reactivity in Houston**

J. Jolly, S. McDowell, B. Kurka, J. Neece, F. Mercado, G. Cantú  
January 23, 2004

### **Executive Summary**

The work presented here points out that ethylene and propylene are generally the most important contributors to total reactivity-weighted concentration in Houston, and that some classes of alkanes are often very important contributors as well. The work done here also shows that pentanes, butanes, and alkanes consistently make up 6% to 9% each of the composition of reactivity-weighted VOC (Volatile Organic Compounds) concentration for Photochemical Air Monitoring Site (PAMS) VOC compounds. This level of contribution is often greater than the contribution from butenes or 1,3 butadiene (both designated as highly-reactive VOCs (HRVOCs)). Even though these three groups of compounds (pentanes, butanes, and alkanes) have significantly lower reactivities than currently defined HRVOCs, their high ambient concentrations (14%, 16%, and 18%, respectively, of PAMS VOC concentration at Clinton, when all hours are ) relative to the ambient concentration of HRVOCs (2% to 3% for each of each of four compounds) provide a high contribution to overall air mass reactivity.

### **Introduction**

The Data Analysis Team was asked to analyze the Houston emission inventory to explore the possibility of reducing emissions of VOCs. These reductions would be in addition to the approximately 64% reduction of HRVOCs that was mandated as part of the December 2002 SIP (TCEQ, 2002). Specifically, the team was asked if such additional reductions could be achieved through either or both of the following means:

- 1) the addition of one or more compounds to the list of regulated HRVOCs in the area (presently this includes ethylene, propylene, butadiene, and butenes in Harris County, and ethylene and propylene in the surrounding seven counties);
- 2) identifying and quantifying other potential VOC reductions that may be gained simultaneously as companies reduce their emissions of the regulated HRVOCs.

This paper discusses both of these means for reducing VOCs.

### **Methods**

The team started by examining data from the 2000 emissions inventory, both point and non-point sources, in the area. Table 1 shows these data.

Point source inventory figures in this table are adjusted upward. These adjustments were made to terminal olefin species only, and were developed by comparing ratios of terminal olefins to NO<sub>x</sub> from airplane flights conducted during the TXAQS 2000 Study to the same ratios (on a molar basis) from area plants. The original Point HRVOC total was 20 tons, and was increased by a factor of eight, resulting in the 160 tons shown in the table.

The original unadjusted Point Non-HRVOC total was 129 tons, and was increased slightly, resulting in the 143 tons shown in the table. This increase is much less than the Point HRVOC increase, because few of the non-HRVOC species are terminal olefins.

Because VOC emissions from biogenic sources (which totaled 1,713 tons/day) are considered to be part of the natural background, they are excluded from this analysis.

<b>Table 1: VOC Emissions in 8-County Houston Area</b>	
Emissions Category	VOC Emissions (tons/day)
On-road Mobile	156
Area + Non-road	241
Point (4 HRVOCs) – Adjusted	160
Point (other VOCs) – Adjusted	143
<b>TOTAL</b>	<b>700</b>
<i>Sources: 1) Gabe Cantu, 12/5/2003, pers. communication (point source figures);  2) Technical Support Document 2, Post-1999 Rate-of-Progress and Attainment Demonstration Follow-up SIP for the Houston-Galveston Ozone Nonattainment Area, Dec. 13, 2002</i>	

### **Analysis of Important VOC Species**

Analysis principally focused on quantifying reactivity-weighted species composition (of VOCs) of air masses at the two long-term Automated Gas Chromatograph (Auto-GC) monitors in the area, Deer Park and Clinton, using data from 1998-2002. This analysis was also performed on five other Auto-GCs in the area, which operated to a lesser extent during this period. Also, results of an earlier study looking at long-term reactivity-weighted VOC concentration at 17 VOC canister sites in the Houston area (Fang et al, 2003) are included for comparison with the Auto-GC work discussed here. Finally, this paper addresses some preliminary factor analysis work done using early morning data from Deer Park for 1998-2002.

In order to determine which VOCs were significant, the hourly concentration data for each compound was converted to a reactivity-weighted concentration using the Maximum Incremental Reactivity (MIR) scale (Carter, 2002). This was done by multiplying each compound's concentration in ppbC times an MIR conversion factor. This conversion factor is equal to the MIR value for the compound times the ratio of its molecular weight to the molecular weight of ozone; this product is then divided by the number of carbon atoms in the compound.

The MIR scale is a measure of how many grams of ozone can be formed from the addition of one gram of the subject VOC, under ideal conditions. There are approximately 55 PAMS VOCs measured by the Auto-GCs; to facilitate analysis, these were binned into one of sixteen VOC groups, which were used to represent compound classes. The reactivity-weighted concentration for each of these sixteen groups was found by summing the reactivity-weighted concentration of all of the compounds falling within that group. Table 2 shows these compound groups along with the mean MIR for each group. For each hour, reactivity-weighted concentrations for each species were summed by VOC group, resulting in contributions to total reactivity-weighted concentration for the hour from each of the 16 groups.

Such species composition analyses were performed for the following conditions:

- all hours in the entire five-year period;
- morning hours of the entire period, when emissions may have been less likely to have traveled long distances;
- hours when the air mass was deemed highly reactive;
- morning hours on days in which one or more monitors in the eight-county area exceeded the eight-hour ozone standard (85 ppb); and,
- hours during which ozone concentrations exceeded the one-hour ozone standard (125 ppb).

The contribution to total reactivity from each VOC group was determined by taking the median of all subject hours.

<b>Table 2: VOC Group Definition</b>		
<b>VOC Group Name</b>	<b>Compounds in the Group</b>	<b>Average MIR Values for Species in Group</b>
Propylene	Propylene	11.58
Ethylene	Ethylene	9.08
Butadiene	1,3-Butadiene	13.58
Butenes	1-Butene, c-2-Butene, t-2-Butene	12.48
Pentenenes	1-Pentene, c-2-Pentene, t-2-Pentene	9.42
Isoprene	Isoprene	10.69
C2C3	Ethane, Propane, Acetylene	0.71
Butanes	n-Butane, Isobutane	1.34
Pentanes	n-Pentane, Isopentane	1.60
Alkanes	n-Hexane, 2-Methylpentane, 3-Methylpentane, 2,2,4-Trimethylpentane, 2,3,4-Trimethylpentane, n-Heptane, n-Octane, n-Nonane, n-Decane, 2-Methylheptane, 2-Methylhexane, 3-Methylheptane, 3-Methylhexane, 2,2-Dimethylbutane, 2,3-Dimethylbutane, 2,3-Dimethylpentane, 2,4-Dimethylpentane	1.39
Toluene	Toluene	3.97
Xylenes	o-Xylene, m- + p-Xylene	5.87
Trimethylbenzenes	1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene	9.89
Aromatics	Benzene, Styrene, Isopropyl Benzene (Cumene), Ethylbenzene, m-Diethylbenzene, p-Diethylbenzene, n-Propylbenzene	3.13
Cyclos	Cyclopentane, Cyclohexane, Methylcyclopentane, Methylcyclohexane	2.14
Ethyltoluenes	o-Ethyltoluene, m-Ethyltoluene, p-Ethyltoluene	6.61

### Analysis Step 1: All Hours / Morning Hours

To start, all available data in the five-year period were analyzed, at Clinton and Deer Park. Figure 1-1 shows the median composition by VOC group in the air at Clinton, for all hours between 1998 and 2002. In this as well as all other pie charts, the four regulated HRVOCs (ethylene, propylene, butadiene, butenes) are listed as the first four groups, starting at the top and moving clockwise. At Clinton, they compose 35% of total VOC reactivity in the air. The next three largest contributors to reactivity are alkanes, pentanes, and butanes, each contributing 9% of total reactivity. The large contributions of these last three groups is surprising, given that their mean group reactivities are near the bottom of the sixteen VOC groups being studied (Table 2).

Figure 1-2 is similar to Figure 1-1, except it includes only morning hours (0500-0959) at Clinton during the months April through October. Here, the composition is slightly different. The regulated HRVOCs contribute 37% of total reactivity-weighted concentration, and alkanes, pentanes, butanes, and xylenes are the next four largest contributors, each composing between 7 and 9% of the total reactivity.

At Deer Park, when all hours are included (Figure 1-3), one sees a different composition. Propylene and ethylene are more important, together contributing a third of the median reactivity-weighted concentration. When butadiene and butenes are added to this, 42% of total reactivity-weighted concentration is accounted for. The next four contributors are C2C3, butanes, pentanes, and alkanes, each with 7-8% of total reactivity.

When just morning hours are included at Deer Park (Figure 1-4), the composition is similar to Figure 1-3. The regulated HRVOCs again compose 42% of total reactivity-weighted concentration; C2C3, butanes, pentanes, and alkanes are again the next four contributors, each one contributing between 7 and 8% of total reactivity.

### Analysis Step 2: High Reactivity Hours

The next step was to look at the contribution by VOC group when only those hours with highly-reactive air masses were included. This is important because, all other things being equal, such air masses are more conducive to ozone formation than are lower-reactivity air masses. For the purposes of this study, a highly-reactive air mass is defined as one whose aggregate MIR reactivity-weighted concentration was equal to or greater than 166. This represents the 90<sup>th</sup> percentile of aggregate reactivity-weighted concentration of all measurements captured by NOAA and DOE aircraft during the TXAQS 2000 Field Study.

Figure 2-1 shows contribution to reactivity-weighted concentration by VOC group at Clinton during hours of high reactivity. At this monitor, there are some subtle differences in VOC contributions when only high-reactivity hours are analyzed versus when all hours were examined (Figure 1-1). The regulated HRVOCs combined contribute a little more (38% vs 35%) than when all hours were considered. The next three contributors, as before, are butanes, pentanes,

and alkanes. In spite of their low mean reactivities, their contribution to total reactivity-weighted concentration is even greater (30% vs 27%) during high-reactivity hours than during all hours.

At Deer Park (Figure 2-2), the composition changes dramatically when only high-reactivity hours are considered, as compared with all hours (Figure 1-3). Propylene and ethylene become dominant, together contributing 56% of total reactivity. The next highest contributors are the same less-reactive groups we see at Clinton and before at Deer Park: butanes, pentanes, and alkanes. Their contributions are 5-7% per group. Butadiene and butenes, the other HRVOCs, contribute just 1 and 4%, respectively, at this monitor.

#### Analysis Step 3: High Ozone Hours/Days

Next, air mass composition at the two monitors, during periods of elevated ozone, was analyzed. Analysis was done only on hours when ozone exceeded the 1-hour ozone NAAQS and the hour prior to the first ozone exceedance hour of each subject day. The prior hours were included because it appears that VOC concentrations often “ramp up” one hour before ozone exceeds.

At Clinton, there were 38 one-hour ozone exceedance days between 1998 and 2002; all but one had associated VOC sampling data. The VOC composition for the subject hours on these 37 days is shown in Figure 3-1. One can see a large shift in importance of several of the VOC groups. Ethylene is the most important species, at 20% of total reactivity-weighted concentration. The importance of pentanes and butanes in total reactivity increases in this analysis; the two groups’ contributions are 16% and 12%, respectively. Propylene (11%) and alkanes (9%) are the next two most important groups. While the data set is smaller (110 hours) than those of the other Clinton analyses presented earlier, these results reinforce the earlier findings of the importance of some of the less-reactive VOC groups.

At Deer Park, there were 45 one-hour ozone exceedance days in the five-year period; 36 of these had corresponding VOC data, yielding 128 hours of data for analysis. Figure 3-2 shows the VOC composition for these hours at Deer Park. One can see that ethylene and propylene -- with a combined 63% - - have become even more important contributors to total reactivity as compared to the earlier analyses. Again, butanes, pentanes, and alkanes are the next contributors, with 8%, 7%, and 6%, respectively. No other compounds contribute more than 4%.

#### Analysis Step 4: Other Monitors

The majority of analyses focused on the two long-term monitors in the Ship Channel. However, there are data available from other monitors in that area. Table 3 shows that in the period 1998 through 2002, five other monitors were on-line part of the time. All were located in Harris County; there were no Auto-GCs or other continuous VOC monitors operating elsewhere in the eight-county area during that time. Clinton and Deer Park provided about two-thirds of the total Auto-GC data gathered during this time.

<b>Table 3</b> <b>Houston-Galveston Auto-GC Monitors, 1998-2002</b> <b>Hours of Operation by Year*</b>						
	1998	1999	2000	2001	2002	Total
Clinton	912	899	937	735	866	4349
Deer Park	817	825	714	885	864	4105
Bayland Park	534	882	516	--	--	1932
Aldine	--	--	194	499	--	693
Channelview	--	--	--	326	560	886
HRM 3 - Haden Rd	--	--	--	320	--	320
HRM 7 - Baytown	--	--	--	264	--	264
Total	2263	2606	2361	3029	2290	12,549
*April 1-October 31 of each year; hours 5-9						

Figures 4-1 through 4-5 show morning (0500-0959) reactivity-weighted concentration by VOC group at the five other monitors in Table 3. This analysis included all available morning hours at each monitor between April and October inclusive. Ethylene and propylene are the top two contributors to reactivity-weighted concentration at all five of these monitors. At Aldine, trimethylbenzenes, xylenes, toluene, alkanes, pentanes, and butanes are the next most important groups, with contributions from 6%-9%. At Channelview, butanes (10%), butenes (8%), alkanes (7%), and pentanes (7%) follow ethylene and propylene. At Bayland Park, the three alkane classes together with trimethylbenzenes each contribute 8% to total reactivity-weighted concentration. At HRM 3 (Haden Road), the three alkane classes plus toluene and butenes each contribute 7%-9% of total reactivity-weighted concentration. At HRM 7 (Baytown), butadiene is more important to total reactivity-weighted concentration (9%) than at other monitors, but after the regulated HRVOCs, butanes, pentanes, and alkanes (7%-9% each) are the most important groups.

After looking at each monitor individually, all data from all monitors for the entire five-year period were combined and analyzed. Figure 4-6 includes all morning hours in the period 1998-2002. Propylene and ethylene are the top two compounds, together contributing 31% of total reactivity-weighted concentration. The other two HRVOCs, butenes and butadiene, add 2% and 6% respectively, which is less than what is contributed by alkanes, pentanes, butanes, toluene, xylene, and trimethylbenzenes (each one between 6% and 8%).

Figure 4-7 contains only those hours from Figure 4-6 where total reactivity-weighted concentration was at least 166. Here, propylene and ethylene both become more important parts of total reactivity-weighted concentration, totaling 37%. Alkanes, pentanes, and butanes, at 8% apiece, are the next most important contributors, more so than the other two HRVOCs.

Figure 4-8 also contains a subset of hours from Figure 4-6: those hours for days where peak 8-hour ozone average in the eight-county area was greater than 85 ppb. As with the previous two figures, ethylene and propylene are the two most important species, reactivity-wise, though their contributions (33% combined) are less than on high-reactive morning hours.

The data from the other five monitors individually, as well as when all monitors are combined, reflect a story consistent with that seen at Clinton and Deer Park: ethylene and propylene are the two most important contributors to total reactivity, and butanes, pentanes, and alkanes are consistently the next most important contributors.

#### *Analysis Step 5: Relative Importance of Constituents of Butanes, Pentanes, and Alkanes*

Thus far, perhaps the most noteworthy finding of this study is that after the regulated HRVOCs, butanes, pentanes, and alkanes appear to be the most important VOC contributors to total reactivity in the air in Houston. This is noteworthy because they are so unreactive; only one of the sixteen VOC groups studied in this analysis is less reactive.

Both the pentanes and butanes groups comprise two compounds; alkanes has 17 constituents. What is the relative importance of the different species in each of these groups?

Figure 5-1 shows the breakdown of butanes constituents, by median contribution to group reactivity-weighted concentration, at Clinton during the 110 hours of high ozone used in Figure 3-1. The two constituents, n-butane and isobutane, are nearly equal in importance. A seasonal distribution of these two compounds has been observed at two or more monitors in the area. Data from the Bayland Park monitor are shown in Figure 5-2. This seasonal effect may be due to the different concentrations of these two species in summertime reformulated gasoline (RFG) in Houston (in use from May 1 through September 15) versus wintertime RFG. It is probably important to separate the effect of season on concentration before determining the relative importance of the two butanes.

Figure 5-3 shows the contribution to reactivity-weighted concentration of the two pentanes compounds, n-pentane and isopentane, at Clinton during the 110 hours of high ozone used in Figure 3-1. Isopentane composes 68% of the group's reactivity-weighted concentration during these hours. Figure 5-4 shows the same breakdown, but for the 17 species which compose the alkanes group. Here it can be seen that the three hexane constituents (n-hexane, 2-methylpentane, and 3-methylpentane) together contribute well over half of the total group reactivity-weighted concentration.

Figures 5-5 and 5-6 show the same breakdowns for pentanes and alkanes, but for Deer Park



ozone exceedance hours rather than Clinton exceedance hours. As at Clinton, isopentane is the dominant pentane (66% of group reactivity-weighted concentration), and the three hexanes contribute about the same amount of combined reactivity in the alkanes class (65%) as they do at Clinton.

#### Analysis Step 6: Preliminary Factor Analysis of Deer Park Data

Factor analysis was performed on Deer Park Auto-GC data for hours 0000-0559 during the years 1998-2002. This analysis had two goals:

1. To characterize VOC emission sources near the auto-GC;
2. To estimate what fraction of ordinary VOC emissions might coincidentally be reduced by existing HRVOC controls.

Factor analysis is a statistical method similar to principle component analysis, but better suited for these data. Principle component analysis searches the data for the largest component species and attempts to relate all other component species to it. However, it is easily confounded if two sources, usually sampled at different times, have the same principle component, e.g. if one source emits ethylene and propane, and another emits ethylene and butane.

Factor analysis attempts to overcome this problem by assuming the identity of the source or sources being monitored is an unknown variable. Factor analysis searches for clusters of species that always occur together, from one or more sources. Factor analysis could differentiate, for example, between the two hypothetical sources listed in the previous paragraph.

Factor analysis was only able to differentiate a relatively small percent of the actual sources in the area around Deer Park. Data were grouped according to wind direction (each of the four primary directions, with a fifth group representing calm conditions). Thirteen source profiles were identified this way, whereas there are hundreds of sources in the area. Since many of these profiles were similar, all of the data were combined; only three unique profiles resulted. They are listed in Table 4 below.

<b>Table 4</b> <b>Source Profiles when All Wind Directions Combined</b> (values shown are percent by mass)			
<b>VOC Species</b>	<b>Source 1</b>	<b>Source 2</b>	<b>Source 3</b>
Ethane	20	17	16
Ethylene	6	5	7
Isobutane	8	7	8
Isopentane	5	14	6
n-Butane	7	11	8
Propane	16	12	16
Propylene	10	8	14

Each of the profiles consist of the same major components: ethane, propane, propylene, isobutane, n-butane, ethylene, and isopentane. The only difference is in the ratios of these components. While there are major differences in concentration by wind direction, the ratio of VOC species doesn't vary much. This suggests that the density and similarity of sources in the area makes source resolution difficult.

From this limited analysis, it appears the sources of ethylene, propylene, and light hydrocarbons dominate the sources observed.

While a complete study is needed to assign these emissions to specific sources, some very broad suggestions may be in order. Ethane is a major component of natural gas, as well as a refinery product. Propane, isobutane, n-butane, and isopentane are all refinery products, as well as feed stock for propylene and ethylene manufacture. As well, these alkanes are associated with area source emissions (e.g. gas stations) and mobile source emissions.

Future work in this area may need to group data by wind direction with even greater resolution than simply the four primary wind directions. This could help distinguish sources which may have only subtle differences in emission profiles, and could also separate non-point contributions from point sources. Also, some of the ethane and propane emissions may be arriving from outside the area, given their unreactive nature. It may be possible to normalize the data to account for the percent of these species coming in from outside, which would enhance the resolution of the other, more locally-emitted species, and therefore would be a more valuable tool for reconciling the observed concentrations with the emission inventory.

## Comparison of Auto-GC to Canister Analyses

In an earlier study (Fang et al, 2002), data from 1997 through 2001 for 17 different canister sites in the Houston-Galveston area were analyzed in a manner similar to how the Auto-GC were analyzed in this study. Table I-5 from that paper shows the top four VOC group contributors to total reactivity for high reactivity-weighted concentration samples at each monitor<sup>1</sup>. At the monitors, ethylene and/or propylene were the most important, or second most important, contributors 27 out of 34 possible times (17 sites times 2 places).

**Table I-5. Top four compounds contributing to high reactivity at HGA monitors**

Site Name	Compound	%	Compound	%	Compound	%	Compound	%
480391003	Ethylene	87	Propylene	6	Cyclos	2		
481670005	Butenes	20	Propylene	15	Pentanes	12	Pentenes	9
481670014	Propylene	22	Ethylene	19	Butanes	11	Butenes	10
481670053	Propylene	25	Butenes	21	Ethylene	10	Pentanes	10
482010024	Ethylene	13	Propylene	13	Butenes	9	Pentenes	9
482010026	Propylene	36	Ethylene	18	Butanes	10	Butenes	7
482010029	Propylene	19	Ethylene	16	C2C3	11	Butanes	11
482010055	Propylene	16	Ethylene	16	Butenes	10	Butanes	8
482010057	Propylene	17	Ethylene	14	Butenes	13	Butanes	10
482010058	Propylene	60	Ethylene	14	Butenes	8	Pentenes	4
482010061	Propylene	43	Ethylene	16	Butanes	8		
482010064	Butenes	35	Propylene	17	Ethylene	11	Butadiene	9
482010069	Butenes	29	Pentenes	12	Propylene	11	Butanes	10
482010803	Propylene	23	Ethylene	17	Butenes	12	Butanes	10
482011035	Butenes	15	Butanes	15	Propylene	12	Ethylene	10
482011039	Propylene	42	Ethylene	18	Butenes	6	Butanes	6
482011041	Propylene	81	Ethylene	5	Butenes	2	Pentanes	2
<i>Source: Fang et al (2002)</i>								

---

<sup>1</sup>High reactivity samples were defined as those with total reactivity in the 90<sup>th</sup> percentile or greater of all samples collected at a monitor.

## Uncertainties in VOC Emission Levels and Reductions

As mentioned near the beginning of this document, one of the purposes of this study was to determine if caps placed on the regulated HRVOCs, as prescribed in the December 2002 SIP, are resulting in other VOCs being reduced, and if so, by how much.

To analyze such an effect, it is important to discuss how such reductions might actually occur. If a company decides to install an “end-of-pipe” control on an emission point, in order to reduce emissions of one or more of its regulated HRVOCs by 64%, it is possible that any associated emissions at that emission point are also being reduced 64%. Table 4 shows that for the non-HRVOCs in the eight-county area, 57 tons/day, or 44% of the non-HRVOCs, are co-located with the HRVOCs. If these co-located emissions were reduced by 64% thanks to the HRVOC caps, that amounts to an extra 37 tons/day of VOC reductions in the area, simply due to the existing caps.

<b>Table 5: Unadjusted Point Source VOC Emissions (tons/day) in 8-County Area</b>			
<b>VOC Category</b>	<b>Co-Located?</b>	<b>Subtotal</b>	<b>Total</b>
HRVOCs			20
Other VOCs	Co-located	57	129
	Non Co-located	72	
Total VOCs			149

However, the TCEQ rules which address these HRVOCs (30 T.A.C. §§ 115.720 - 115.729) do not require companies to follow a particular control strategy; instead, they simply instruct companies to stay below their caps, as delineated in Tables 6-2.1 and 6-2.2 in the December 2002 SIP. A company may choose to reduce its HRVOCs by process changes, such as equipment modifications, use of different catalysts, or process optimization. It can modify its raw material feedstock, or change its product specifications. Without more information on how companies may be applying these techniques, it is very difficult to quantify the effect on emission rates of the associated VOCs. Reductions in HRVOCs achieved via these techniques may result in similar or smaller reductions in other VOCs, or even increases in some of the associated VOCs.

Additionally, there is variability and uncertainty in the actual emissions of the alkanes, butanes, and pentanes. Concentrations of some of these compounds have been observed at very high concentrations at Clinton – for example, on May 25, 2001, isobutane and n-butane had a combined concentration of 9,913 parts per billion carbon, at 9 pm. This suggests emissions may be occurring at levels much greater than reported. The reportable quantities (RQs) for upset,

maintenance, startup, and shutdown events – i.e., non-routine emissions – for the compounds in these three classes remain at 5000 lb per compound per event. Given errors in emission estimation, some very large emission events may remain undocumented. (An analysis of an upset release on 9/20/99 showed that the mass of release was many times larger than what was reported.) Furthermore, recent work by TCEQ staff which compared the inventory to ambient VOC:NOx ratios for 12 VOC groups found that the butanes emission inventory seems to be in considerable error not only for point sources, but for non-point sources as well.

Finally, given the large number of gasoline refineries (point sources) and motor vehicles (mobile sources) in the Houston area, it may be difficult to ascertain what portion of some VOC concentrations are being caused by point sources as opposed to mobile sources.

## **Conclusions**

The work presented here points out that ethylene and propylene are generally the most important contributors to total reactivity-weighted concentration in Houston, and that some classes of alkanes are often very important contributors as well. This is consistent with earlier work (Estes et al, 2002) which looked at both OH and MIR reactivity for all available Auto-GC data from the seven TCEQ-operated monitors which have operated in the area. This is also in agreement with work done using canister data in the area (Fang et al, 2002).

This study also points out the contribution to reactivity-weighted concentration made by butanes, pentanes, and C6+ alkanes. This contribution from these classes is often greater than the contribution from butenes or 1,3 butadiene (both designated as HRVOCs). Even though these three groups of compounds (pentanes, butanes, and alkanes) have significantly lower reactivities than currently defined highly reactive VOCs, their high ambient concentrations (14%, 16%, and 18%, respectively, of PAMS VOC concentration) relative to the ambient concentration of HRVOCs (2% to 3% for each of each of four compounds) provide a high contribution to overall air mass reactivity. These high contributions were observed in all phases of the analyses, including studies of data from 1998 to 2002 from each monitor and all monitors together of all hours, early morning hours, high reactivity hours, and high ozone hours.

Any analysis of potential cuts in alkanes must consider at least two major differences between them and the HRVOCs. First, mobile and area sources are important contributors of these emissions, as well as point sources; control strategies aimed at reducing alkanes would probably have to include all of these sources. This could be more difficult than simply getting reductions from point sources.

Additionally, alkanes react much more slowly than do HRVOCs in the ozone formation process, and it is unclear whether reducing their reactivity by a certain amount would net the same benefit in reducing ozone to that gained by reducing HRVOC reactivity by an equal amount. It may be necessary to do photochemical modeling to determine whether this is the case.

## Future Work

In addition to studying the viability of VOC cuts targeted at these compounds, there are at least two other avenues which could be explored. The first is the further use of factor analysis or other sophisticated data analysis tools to help determine sources of the VOCs in the air. This technique may enable analysts to determine the sources of butanes, pentanes, and alkanes, which could help evaluate the feasibility of controlling these compounds. Another way in which the research could be expanded is by using the data from the Enhanced Industry Sponsored Monitor (EISM) network, a group of seven privately operated Auto-GC monitors in Harris, Galveston, and Brazoria counties. These monitors have been on-line since June 2003; at this time, validated data ranges from two to four months, depending on the monitor. These data have already unearthed findings about sources in the Houston area that were not known before. When more validated data are available, this analysis may be expanded to include them.

Finally, a speciated non-point emissions inventory – mobile, nonroad, and area – in order to compare with the speciated point source inventory would be useful. That way, targeted cuts focusing on those compounds that play the most significant role in contributing to air mass reactivity could be analyzed and optimized.

## References

Texas Commission on Environmental Quality. *Revisions to the State Implementation Plan for the Control of Ozone Air Pollution. Post-1999 Rate of Progress and Attainment Demonstration Follow-Up SIP for the Houston-Galveston Ozone Nonattainment Area*, Chapter 6. December 13, 2002. <http://www.tnrcc.state.tx.us/oprd/sips/121302adoption.pdf>

Carter, William P. L. (October 25, 2002). MIR Reactivity Spreadsheet. Available via ftp: <ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r02tab1.xls>

Estes M., S. Wharton, D. Boyer, Z. Fang, J. Smith, S. McDowell, F. Mercado, J. Neece, E. Gribbin, and J. Price (2002). *Analysis of Automated Gas Chromatograph Data from 1996-2001 to Determine VOCs with Largest Ozone Formation Potential*. Attachment 6, Technical Support Document of the TCEQ Executive Director Recommendation for Changes to Chapter 115/117/101 Rules, November 11, 2002. [ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Modeling/Doc/TSD\\_PHASE1/attachment6-agc\\_voc.pdf](ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Modeling/Doc/TSD_PHASE1/attachment6-agc_voc.pdf)

Fang, Z., S. McDowell (2003). *Analysis of canister data for the Houston-Galveston and Beaumont-Port Arthur Areas*. Unpublished report within TCEQ internal document titled “Spring 2003 Data Analysis Projects: Summary and Reports,” edited by TCEQ Data Analysis Team, Technical Analysis Division, 2003.

Figure 1-1: Median Reactivity-weighted Concentration Composition by VOC Group at Clinton

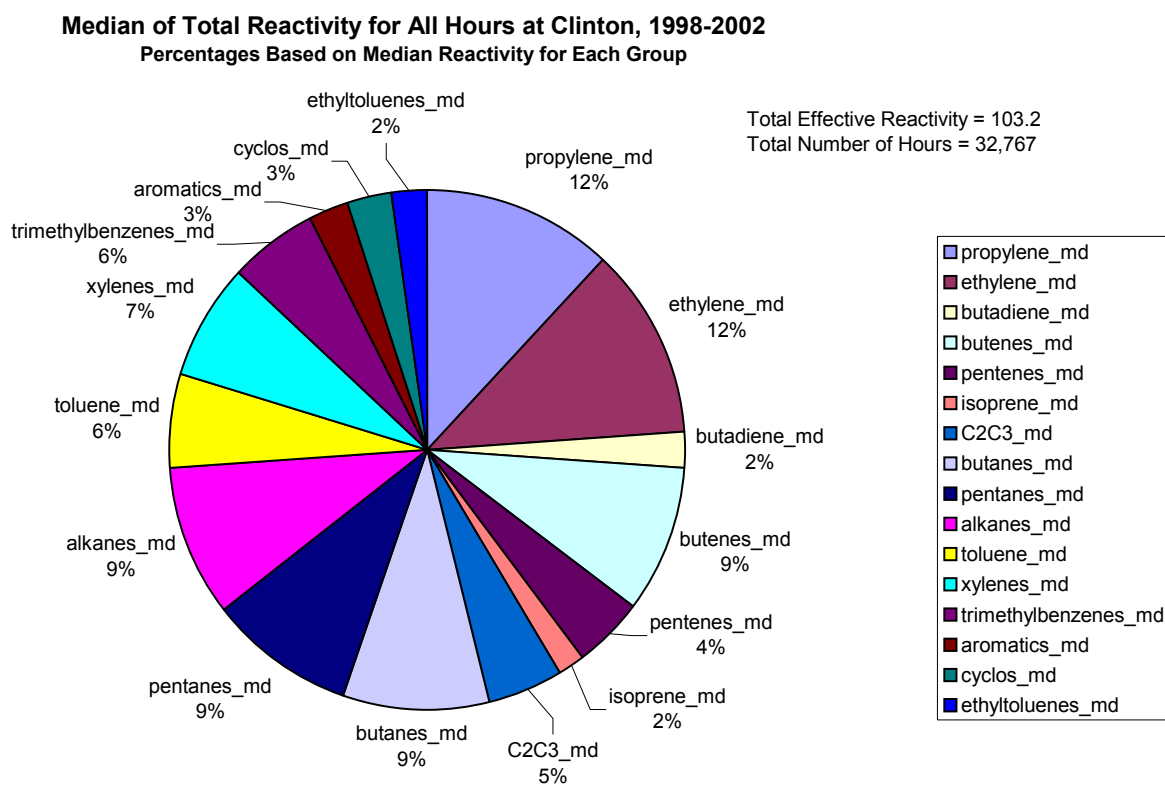


Figure 1-2: Median Reactivity-weighted Concentration Composition by VOC Group for Morning Hours at Clinton, April-October, 1998-2002

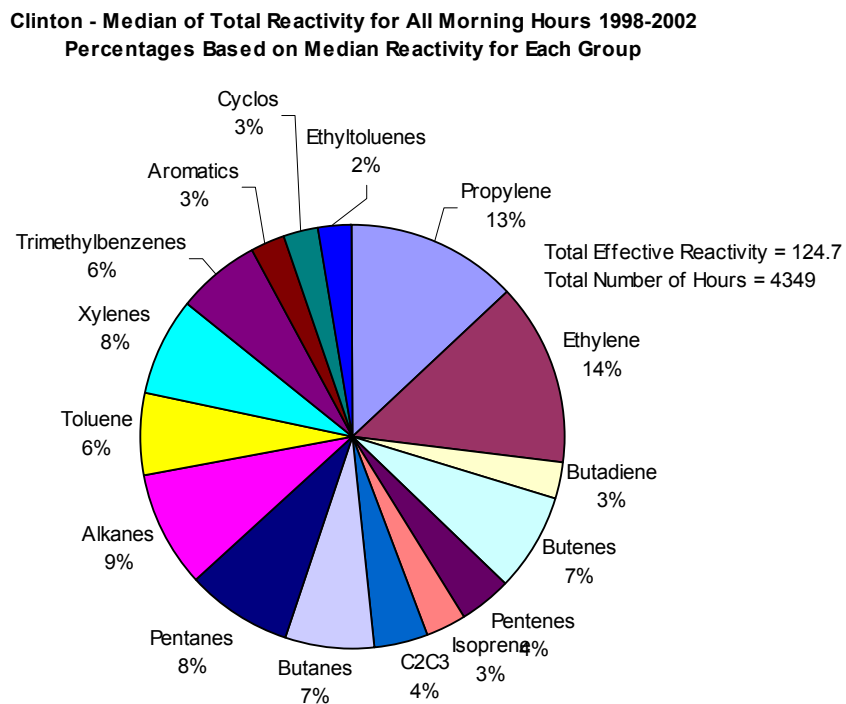




Figure 1-3: Median Reactivity-weighted Concentration Composition by VOC Group at Deer Park

**Median of Total Reactivity for All Hours at Deer Park 2, 1998-2002**  
Percentages Based on Median Reactivity for Each Group

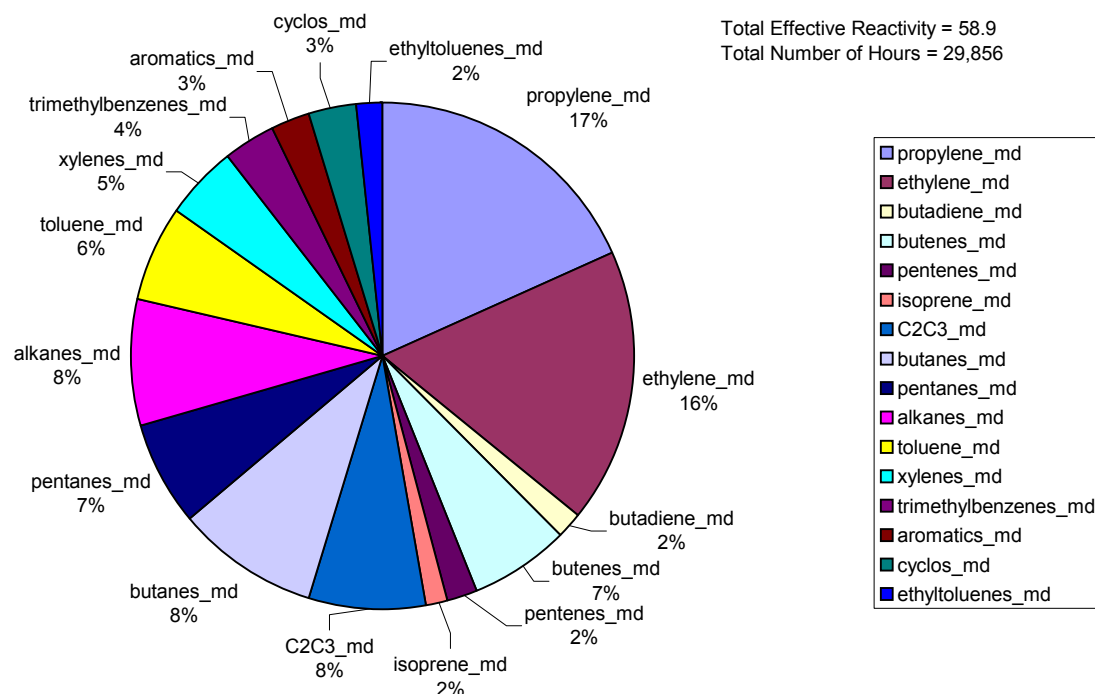


Figure 1-4: Morning Reactivity-weighted Concentration Composition by VOC Group at Deer Park, April-October, 1998-2002

**Deer Park 98-02 Median Reactivity -- All Morning Hours (5-9)**  
**Percentages Based on Median Reactivity for Each Group**

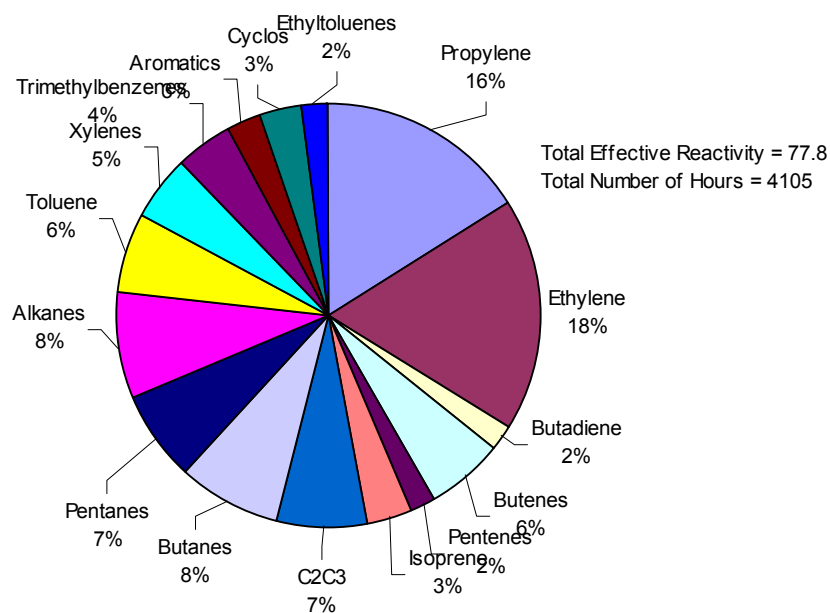


Figure 2-1: Median Reactivity-weighted Concentration Composition by VOC Group at Clinton during High Reactivity Hours

**Median of Total Reactivity for High Reactivity Hours (MIR>166) at Clinton, 1998-2002**  
**Percentages Based on Median Reactivity for Each Group**

Total Effective Reactivity = 249.2  
 Total Number of Hours = 12,668

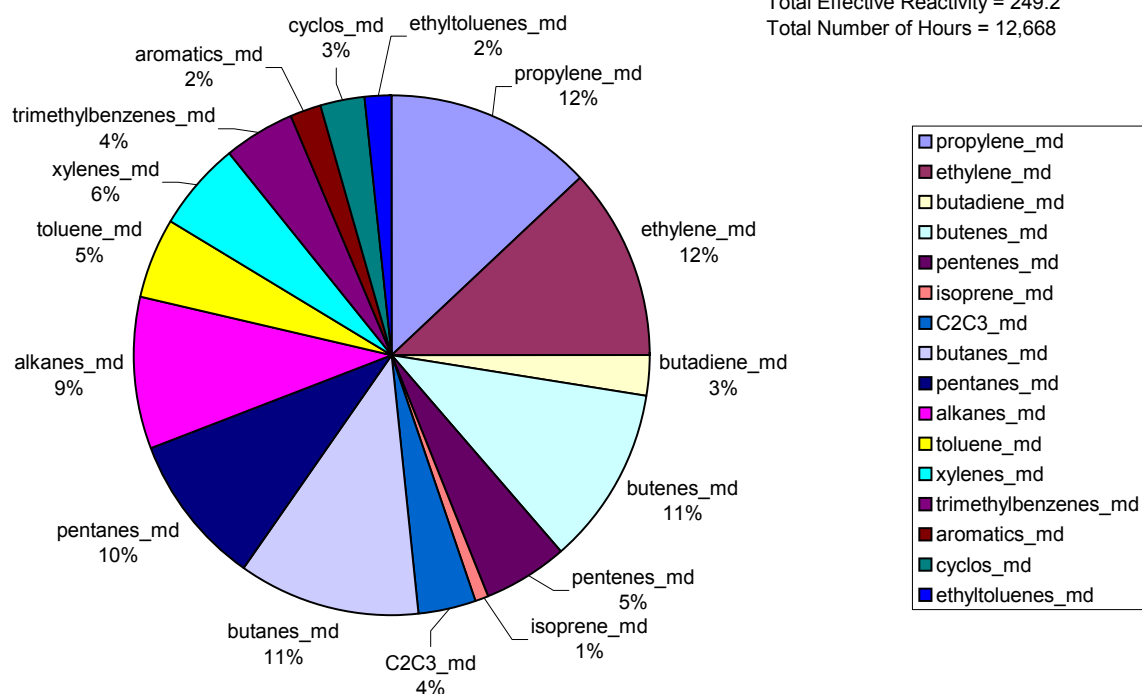


Figure: 2-2: Median Reactivity-weighted Concentration Composition by VOC Group at Deer Park during High Reactivity Hours

**Median of Total Reactivity for High Reactivity Hours (MIR>166) at Deer Park 2, 1998-2002**  
**Percentages Based on Median Reactivity for Each Group**

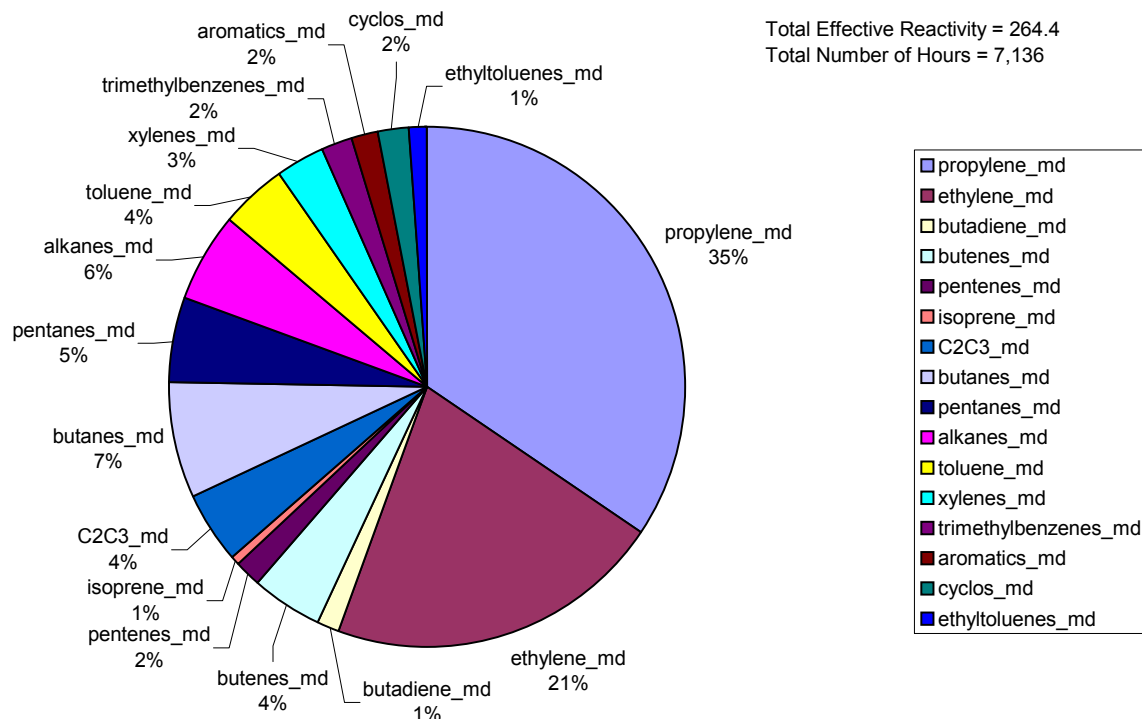


Figure 3-1: Reactivity-weighted Concentration Composition by VOC group during and immediately preceding 1-hour ozone exceedance hours at Clinton

**Median of Total Reactivity at Clinton during One-Hour Exceedances, 1998-2002**  
**Percentages Based on Median Reactivity for Each Group**

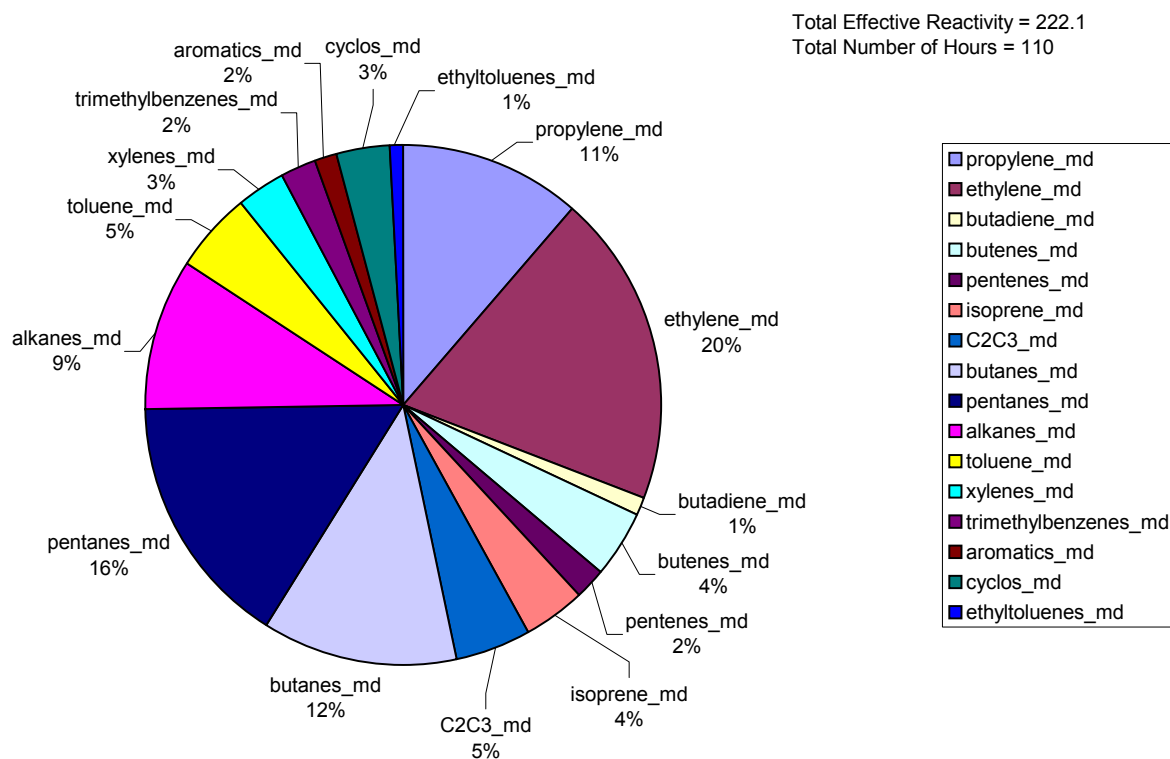


Figure 3-2: Median Reactivity-weighted Concentration Composition by VOC group during and immediately preceding 1-hour ozone exceedance hours at Deer Park

**Median of Total Reactivity at Deer Park during One-Hour Exceedances, 1998-2002**  
**Percentages Based on Median Reactivity for Each Group**

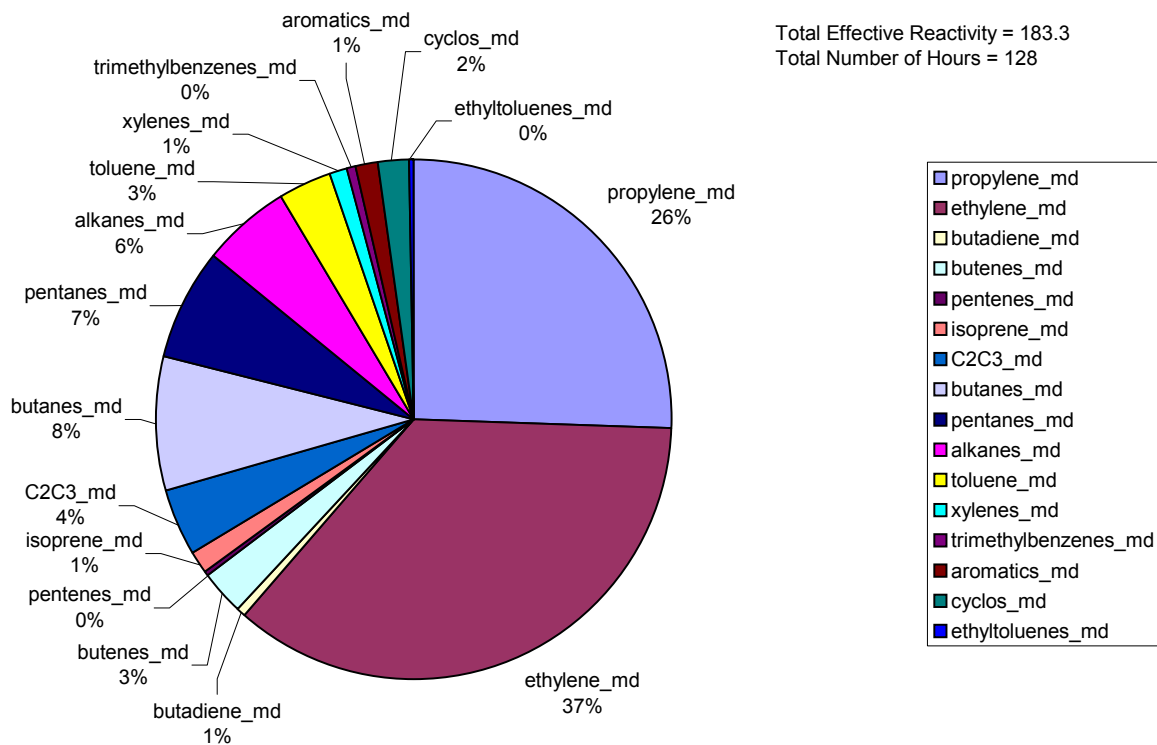


Figure 4-1: Morning Ozone Season Median Reactivity-weighted Concentration Composition at Aldine

**Aldine -- Reactivity for All Morning Hours (5-9), August-October 2000, April-July 2001**  
**Percentages Based on Median Reactivity for Each Group**

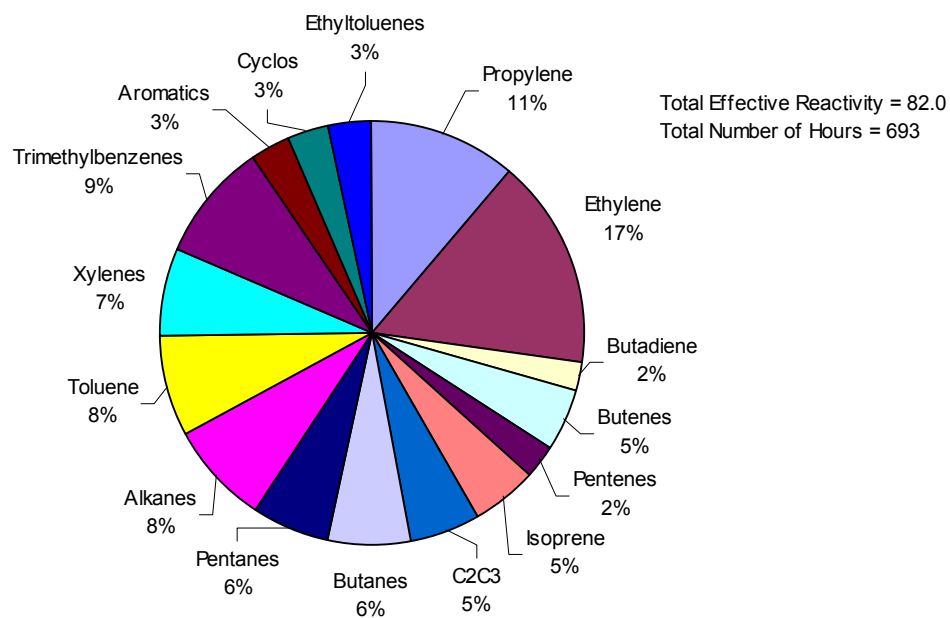


Figure 4-2: Morning Ozone Season Median Reactivity-weighted Concentration Composition at Channelview

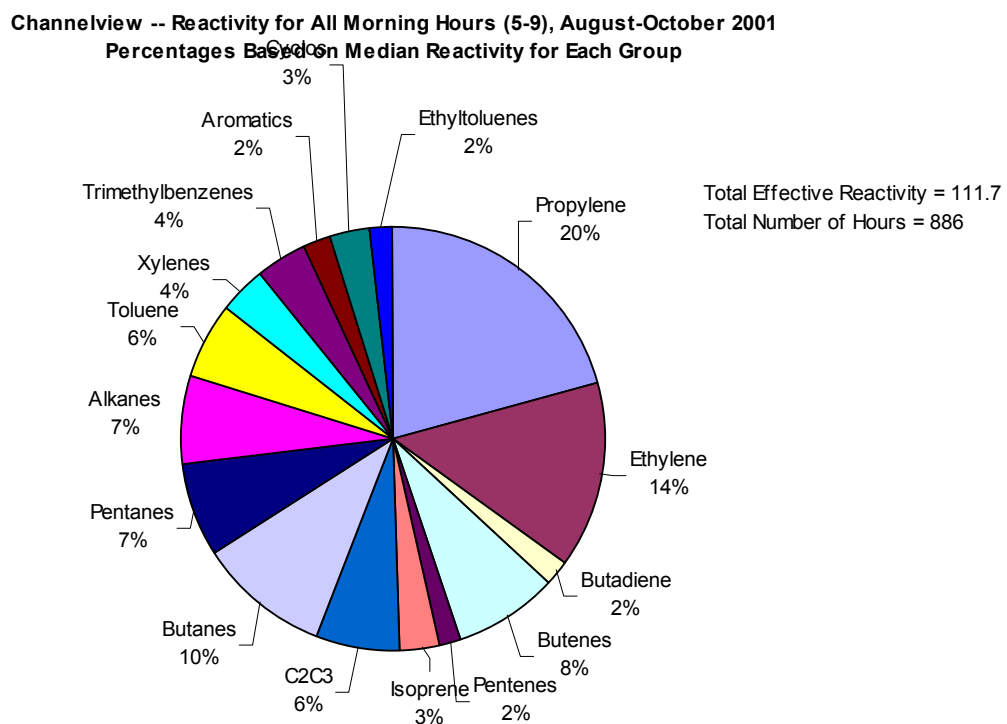




Figure 4-3: Morning Ozone Season Median Reactivity-weighted Concentration Composition at Bayland Park

Bayland Park -- Reactivity for All Morning Hours (5-9), May-October 1998, April-October 1999, April-August 2000  
Percentages Based on Median Reactivity for Each Group

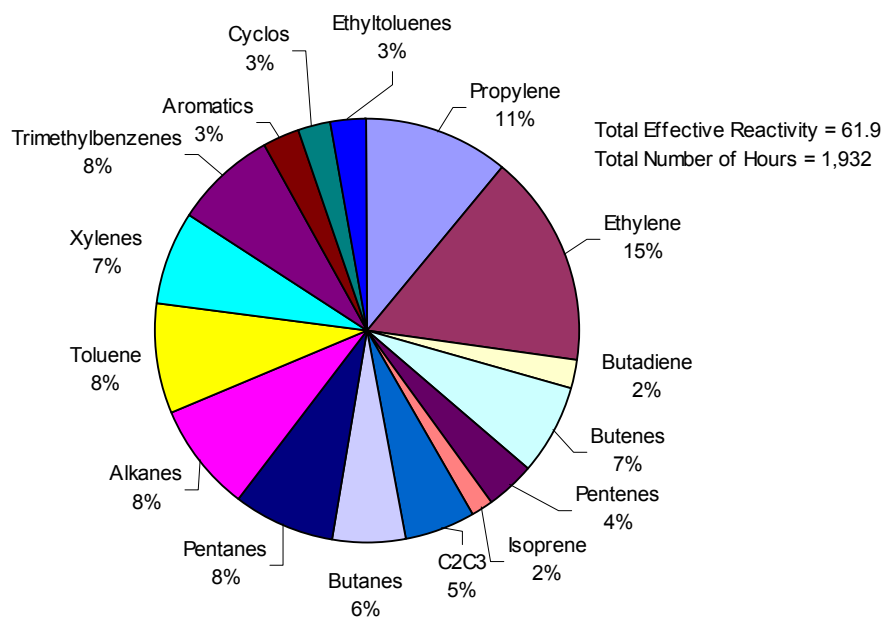


Figure 4-4: Morning Ozone Season Median Reactivity-weighted Concentration Composition at HRM 3

**HRM 3 Haden Rd -- Reactivity for All Morning Hours (5-9), August-October 2001**  
**Percentages Based on Median Reactivity for Each Group**

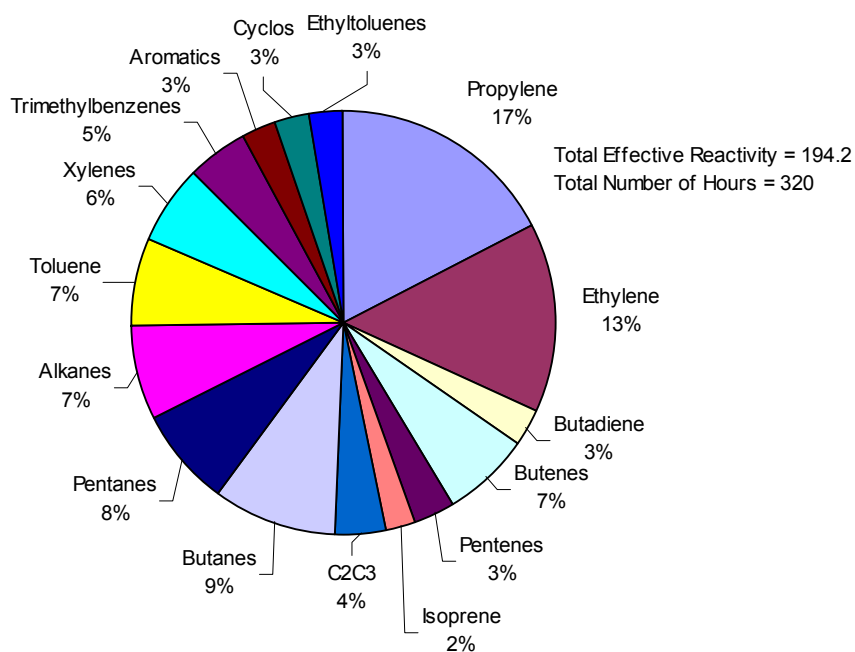


Figure 4-5: Morning Ozone Season Median Reactivity-weighted Concentration Composition at HRM 7

**HRM 7 Baytown -- Reactivity for All Morning Hours (5-9), August-October 2001**  
**Percentages Based on Median Reactivity for Each Group**

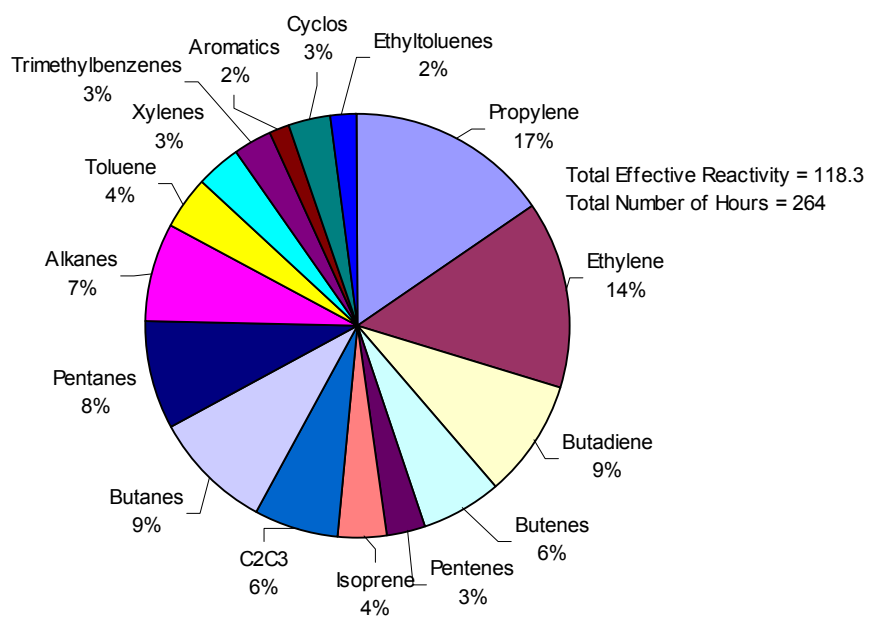


Figure 4-6: Combined Morning Median Reactivity-weighted Concentration Composition for All Monitors, April-October 1998-2002

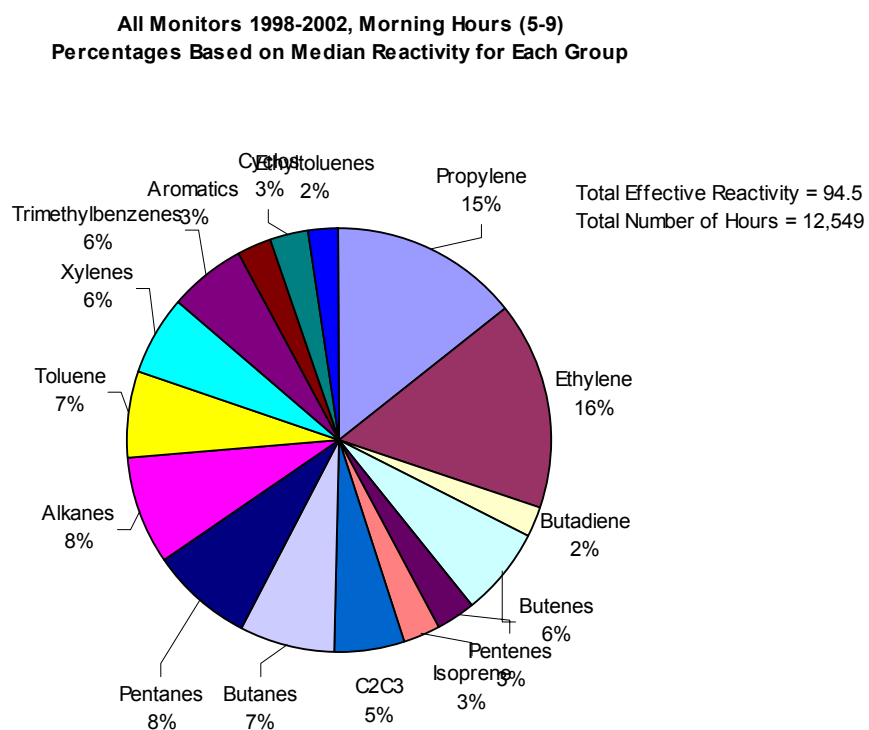


Figure 4-7: Combined Morning Median Reactivity-weighted Concentration Composition for All Monitors during High-Reactivity Hours, April - October 1998-2002

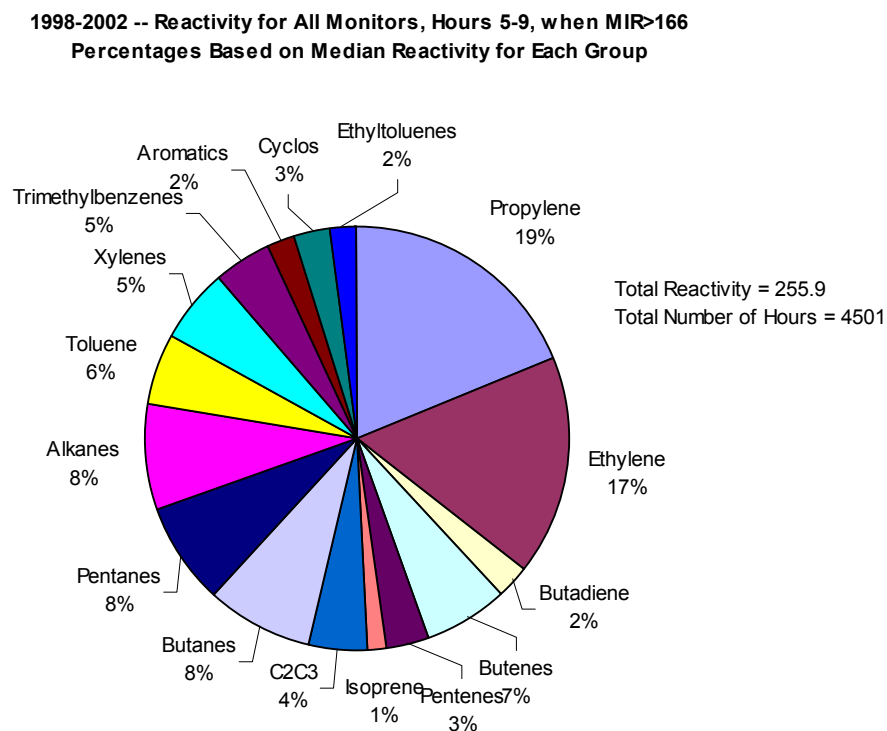


Figure 4-8: Combined Morning Median Reactivity-weighted Concentration Composition for All Monitors on days when Peak Area 8-hr ozone > 85 ppb, April - October 1998-2002

**All Monitors 1998-2002, Morning Hours on days when Peak Area 8hr ozone >85  
Percentages Based on Median Reactivity for Each Group**

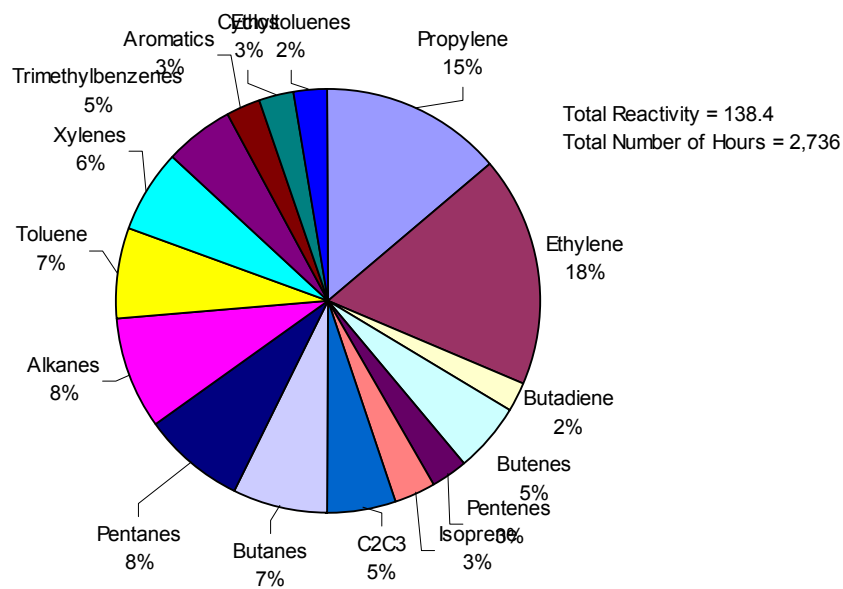


Figure 5-1: Distribution of Butanes constituents, by Median Reactivity-weighted Concentration Composition, during and immediately preceding high ozone hours at Clinton

**Distribution of Butanes during Ozone Events at Clinton, 1998-2002**  
Percentages Based on Median Reactivity for Each Compound

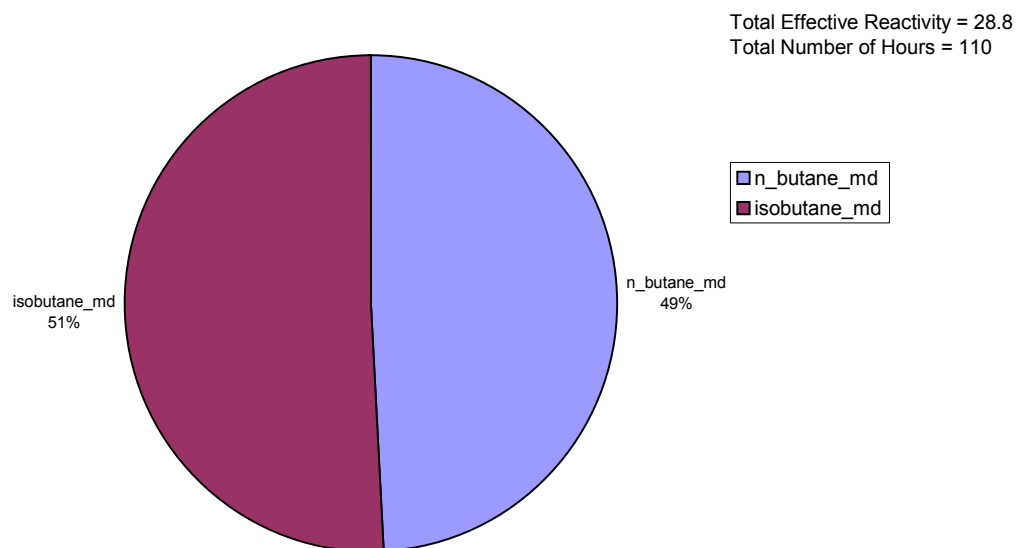


Figure 5-2: Median monthly isobutane/n-butane ratios at Bayland Park, 1998-2000 (*source: M. Estes, 12/8/2003*)

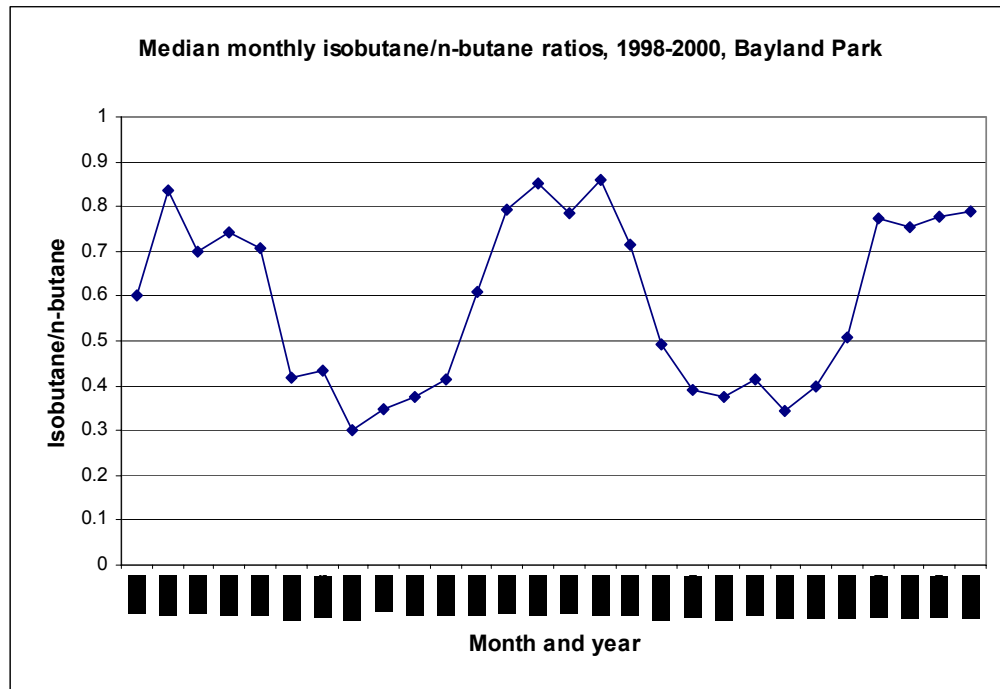




Figure 5-3: Distribution of pentanes constituents, by Median Reactivity-weighted Concentration Composition, during and immediately preceding high ozone hours at Clinton

**Distribution of Pentanes during Ozone Events at Clinton, 1998-2002**  
Percentages Based on Median Reactivity for Each Compound

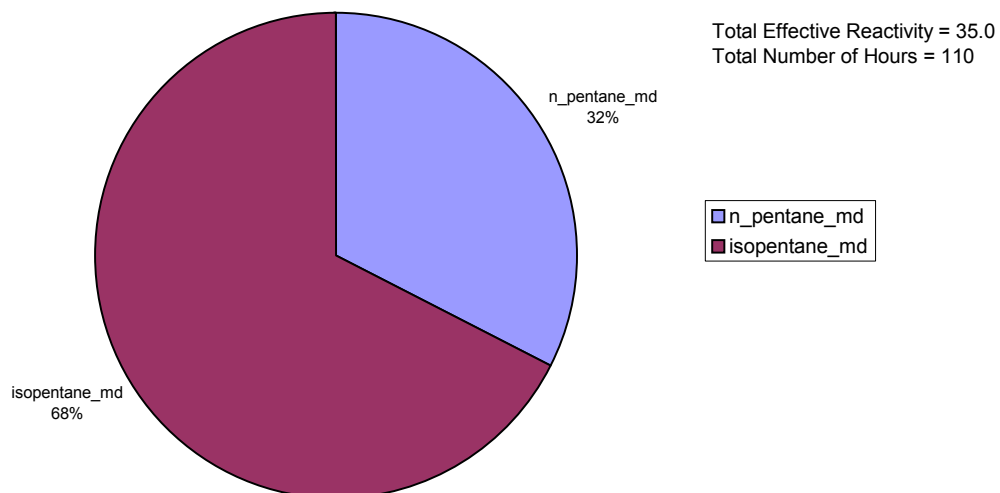


Figure 5-4: Distribution of alkanes constituents, by Median Reactivity-weighted Concentration Composition, during and immediately preceding high ozone hours at Clinton

**Distribution of Alkanes during Ozone Events at Clinton, 1998-2002**  
Percentages Based on Median Reactivity for Each Compound

Total Effective Reactivity = 20.8  
Total Number of Hours = 110

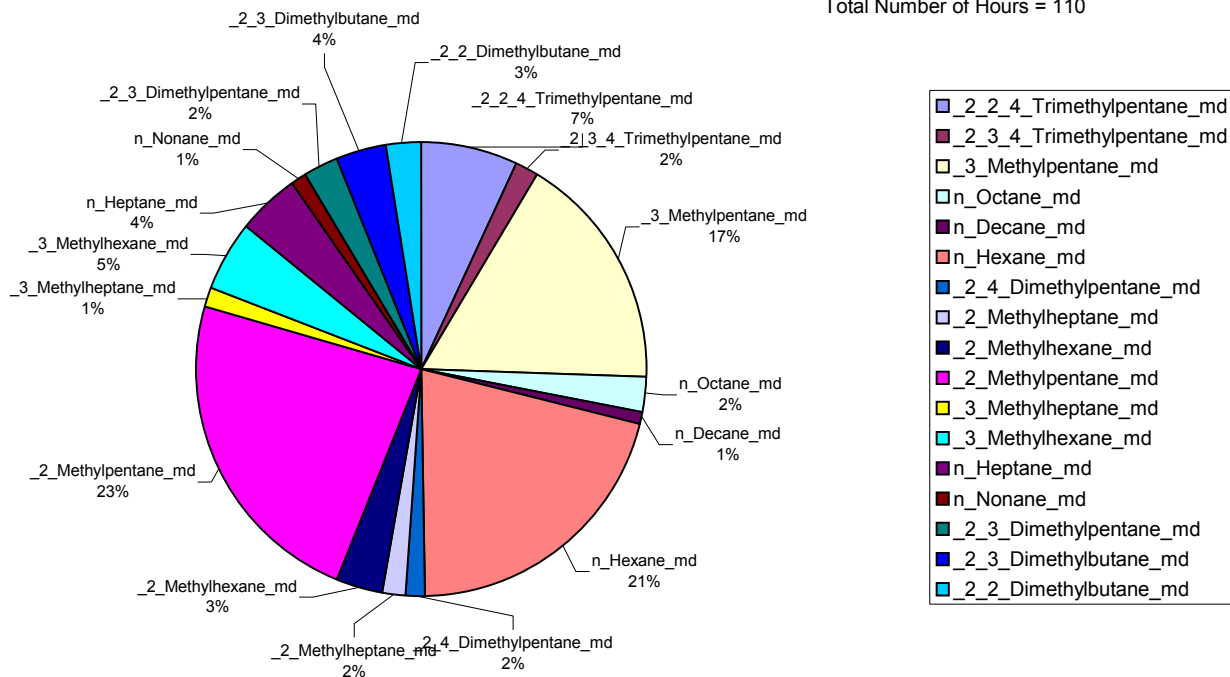


Figure 5-5: Distribution of pentanes, by Median Reactivity-weighted Concentration Composition, during and immediately preceding high ozone hours at Deer Park

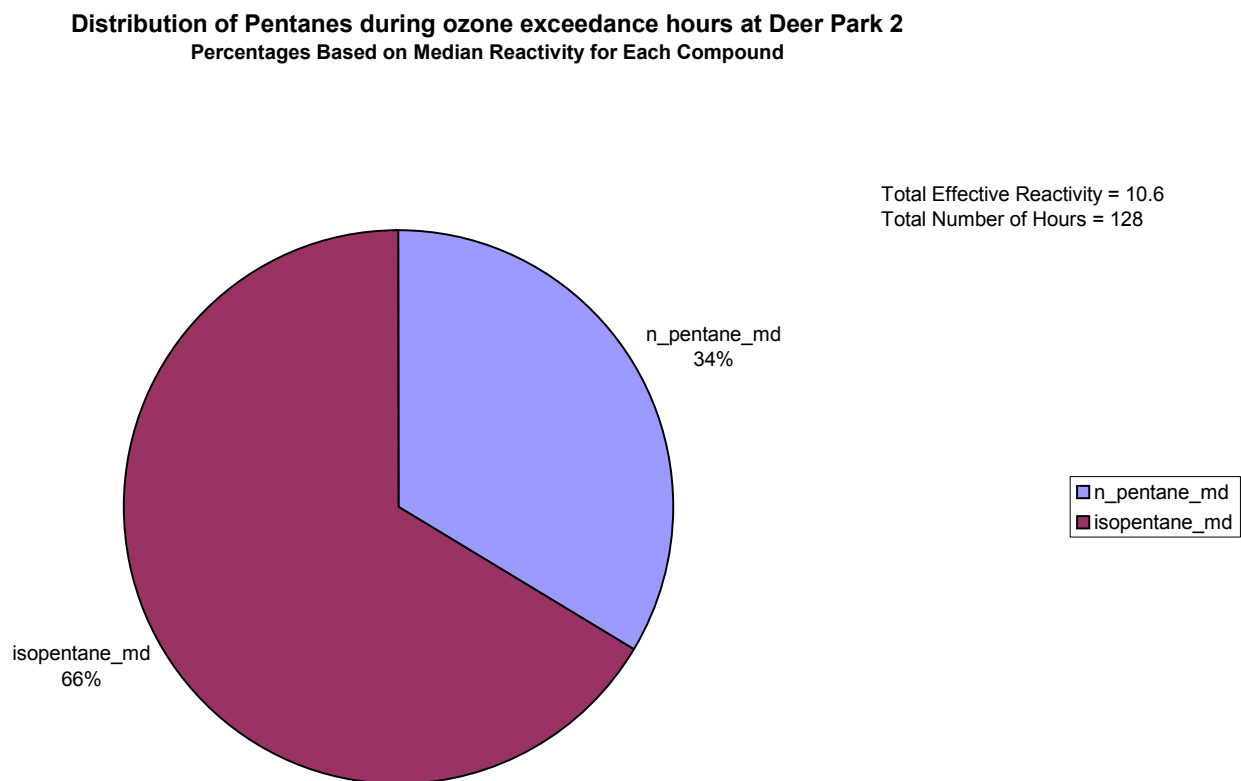


Figure 5-6: Distribution of alkanes, by Median Reactivity-weighted Concentration Composition, during and immediately preceding high ozone hours at Deer Park

